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ADSORPTION OF OXOVANADIUM (IV) FROM AQUEOUS SOLUTIONS BY NANOPARTICULATED HYDROXYAPATITE. THERMODYNAMIC AND KINETIC STUDY

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Abstract

This work reports some interesting thermodynamic and kinetic data dealing with the interaction of oxovanadium (IV) ions with synthetic calcium hydroxyapatite. Their uptake, or ion exchange adsorption, was investigated at different temperatures (range from 288 to 308 K). The amount of the uptake, measured by atomic absorption spectrometry, shows that oxovanadium(IV) ions are adsorbed on the surface of hydroxyapatite by coordination to OH groups. The adsorption is dependent upon pH and temperature, the maximum adsorption being at pH 3.5 and 288 K. The proposed adsorption model is coherent with the experimental data. All the thermodynamic and kinetic parameters were in concordance with the proposed adsorption reaction.

Keywords: hydroxyapatite, oxovanadium (IV), adsorption, thermodynamic study, kinetic study.

Resumen

En este trabajo se reportan interesantes datos termodinámicos y cinéticos relacionados con la adsorción de oxovanadio (IV) sobre hidroxiapatita sintética. Los experimentos de adsorción fueron realizados en el rango de 288 a 308 K. La extensión de la adsorción, medida por espectrometría de absorción atómica, mostró que los iones oxovanadio (IV) fueron adsorbidos en la superficie de hidroxiapatita por coordinación con los grupos OH. La adsorción, dependiente del pH y de la temperatura, alcanzó su máximo a pH = 3,5 y a 288 K. El modelo de adsorción propuesto ajusta los datos experimentales. Los parámetros termodinámicos y cinéticos obtenidos acuerdan con la reacción de adsorción propuesta.

Palabras clave: hidroxiapatita, oxovanadio (IV), adsorción, estudio termodinámico, estudio cinético.

Introduction

The interaction of different species, such as heavy metals, polyelectrolytes, proteins, and other macromolecules with hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (HAP), is of great interest to both fundamental research and technological applications [1-10].

HAP is a major component of hard tissues, namely, bones and teeth and it is an adsorbent material that shows high affinity with polymeric molecules. HAP is often considered a suitable material for making medical implants. In fact, coating metallic implants with bioactive materials, like HAP, may accelerate bone formation on initial stages of osseointegration, improving implant fixation [11-15].

There is a significant difference of properties between natural apatite crystals found in the bone mineral and the conventional synthetic HAP. Bone mineral crystals are in the order of nano-scale range with large surface areas whereas synthetic HAP presents lower ones.

In a previous communication [16], we reported the ability of commercial calcium hydroxyapatite (CAP) to adsorb citric acid, an efficacious and distinctive agent in the demineralization of dental enamel which principal component is HAP, from aqueous solutions.

Literature describing the removal of oxocations from aquatic systems is rather limited [17,18]. Particularly oxovanadium (IV) (VO^{2+}) has been detected in natural waters [19] and as a toxic oxometallic ion, an efficient method of removal from industrial wastes and natural waters is needed. There are some biological and chemical methods which can be applied to uptake this trace element from contaminated waters [20, 21].

In recent years we have reported that VO^{2+} ions are adsorbed on the surface of both synthetic HAP [22] and CAP [23] and the main features of these systems were studied. It is well known that adsorption is strongly governed by the acid-base properties of the adsorbent surface and particularly the OH groups belonging to the surface are responsible for the sorptive properties of these phosphates.

The Langmuir isotherm fits reasonably well the obtained experimental data allowing the determination of the thermodynamic parameters for the VO^{2+}- CAP system [23]. Taking into account the promising results obtained for that system, it results of interest to analyze the interaction of this oxocation with HAP by determining the thermodynamic and kinetic parameters that, as far as we know, no data were previously reported.

In order to go deeper into the knowledge of the physicochemical properties of these systems, we have discussed accurately the mechanism of oxovanadium (IV) fixation on HAP supporting the experimental data by the thermodynamic and kinetics parameters.

Experimental

Hydroxyapatite

Reagents of analytical grade were used in the synthesis of HAP according to the following procedure. Microcrystalline powder was obtained by precipitation in a discontinuous reactor as described by Hayek and Stadlemann [24]. The method, that involves the reaction of equimolar quantities of solutions of $Ca(NO_3)_2.4H_2O$ and $NH_4H_2PO_4$ at pH=12, was chosen because large batches of product can be obtained. The dried solid was calcined at 1073 K for 2 hours. HAP was obtained as white, well-crystallized powder and the characterization of this final product was carried out by X-ray diffraction (XRD) measurements. X-ray powder diagrams were obtained with a Rigaku D-MAX-IIIC diffractometer using CuK_α radiation (Ni-filter) and NaCl and quartz as external calibration standards.

The specific surface area, Sg, of 18 m^2 g^{-1} (by N_2 adsorption-desorption method at 77 K) was determined with a Micromeritics Accusorb 2100E for an outgassing time of 14 h. Chemical composition Ca/P=1.61 (as against the ratio 1.67 for the pure apatite) was determined by inductively coupled plasma spectroscopy in an atomic emission spectrometer associated to an inductively coupled plasma Baird ICP 2070. The point of zero charge, pzc= 6.35, was determined by potentiometric titration in an Orion EA 940.

Oxovanadium(IV) acetate

Reagents of analytical grade were used in Oxovanadium(IV) acetate aqueous solution preparation by dissolving V_2O_5 in boiling acetic acid in presence of hydrazine as reducing agent. The final solution showed an intense blue colour.

Adsorption Experiments

The experimental data for the VO^{2+} ions adsorption on the surface of synthetic HAP were obtained in a batch system consisting of an erlenmeyer flask with a magnetic stirring bar inside to mix the solution. The flask was partially immersed in a bath at 288, 298 or 308 K to maintain constant temperature. Experiments were carried out by contacting 1 g of HAP with 60 mL of a $VO(C_2H_3O_2)_2$ solution with a known metal initial concentration in the range of 3 to 200 mg L^{-1} for 72 hours.

The VO^{2+} concentration was determined after each adsorption experiment, through measurements of V concentration by atomic absorption at a wavelength 318.5 nm. An IL 751 AA/AE, double channel double beam equipment was used.   Measurements of adsorbed vanadium were made on the solution and on the solid residue to corroborate the absence of errors showing an excellent agree. The uptake or change in VO^{2+} concentration values obtained by repetition of the experiments at least twice was reproducible within a range of 5 to 10%. Control experiments showed that there was not uptake of VO^{2+} for its entire range of concentration by the filtering apparatus.

Scanning electron microscopy (SEM) technique was used to observe and analyze the morphology and the particle size of the pure and adsorbed HAP powders. Samples were placed on an adhesive carbon tape coated with gold and observed in a LEO1450VP. Energy dispersive X-ray spectroscopy (EDS) was performed for chemical microanalysis using an EDAX system.

Results and Discussion

Thermodynamics of the adsorption

The adsorption of oxovanadium (IV) ions on HAP surface may be represented by the following equilibrium:

$$VO^{2+} + \equiv OH \quad \rightleftharpoons \quad \equiv -OVO^+ + H^+ \qquad (1)$$
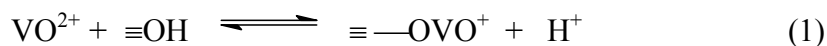
where the formation of the surface complex ($\equiv -OVO^+$) involves the OH groups of HAP. This fact was evidenced by IR spectroscopy [22].

In previous studies we found that the uptake becomes constant after 50 h of contact and remained so for additional periods. The system was kept 72 h to ensure equilibrium in the isothermic assays in order to standardize with the previous data reported for synthetic HAP [22,25] and other materials structurally related [23]. The uptake was time-independent after 72 hours and equilibrium was therefore attained.

The pH effect has been analyzed due to its importance on the adsorption of metal ions on solids. In the present system, the control of this parameter is critical because VO^{2+} ion exists only in a narrow pH range. It was found that HAP is efficient for the adsorption of VO^{2+} at pH values between 2.5 and 3.5. Below pH = 2.5 the adsorbed amount of VO^{2+} is negligible whereas for pH values above 3.5 the superficial phenomena are difficult to analyze because of the hydrolytic process and the precipitation of $VO(OH)_2$. In the studied pH range the positive surface charge of HAP (PZC = 6.35) remains constant [22].

The adsorption isotherms of oxovanadium (IV) ions on synthetic hydroxyapatite from aqueous solutions at pH=3.5 and 288, 298 and 308 K are shown in Figure 1. These are regular Langmuir-type isotherms; consequently, the experimental points can be well fitted according to the expression:

$$C_{ad} = \frac{KCL}{1 + KC} \qquad (2)$$

where C is the equilibrium VO^{2+} concentration ($\mu mol\ L^{-1}$); C_{ad} the adsorbed VO^{2+} concentration ($\mu mol\ g^{-1}$); L the adsorption capacity ($\mu mol\ g^{-1}$) and K the Langmuir adsorption constant ($L\ \mu mol^{-1}$).
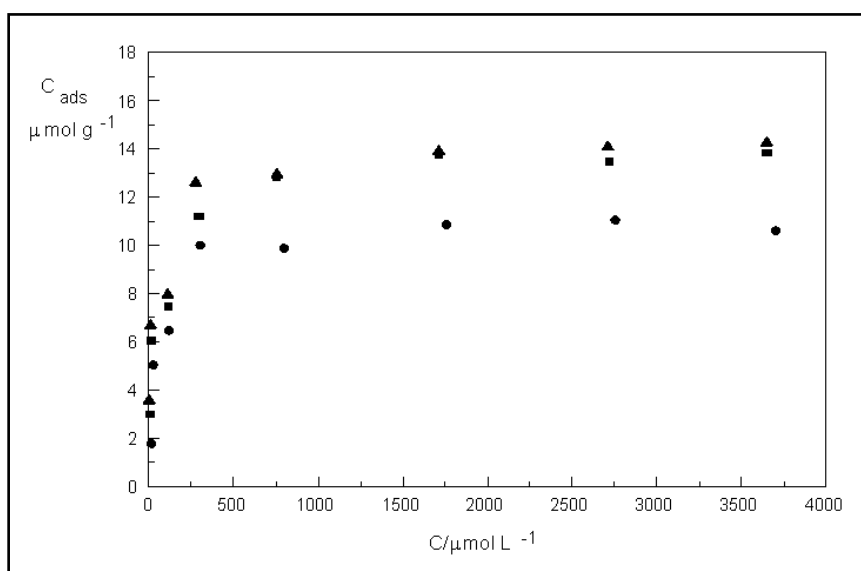

Figure 1. Adsorption isotherms of oxovanadium (IV) by hydroxyapatite from aqueous solutions. Plot of the hyperbolic equation, Eq. (2). (▲) T = 288 K ; (■) 298 K and (●) 308 K.

The full lines in Figure 2 are calculated according Eq. (2) using the Langmuir parameters obtained from the linear expression (Eq. 3) and tabulated in Table 1.

$$\frac{C}{C_{ad}} = \frac{1}{KL} + \frac{1}{L} C \qquad (3)$$

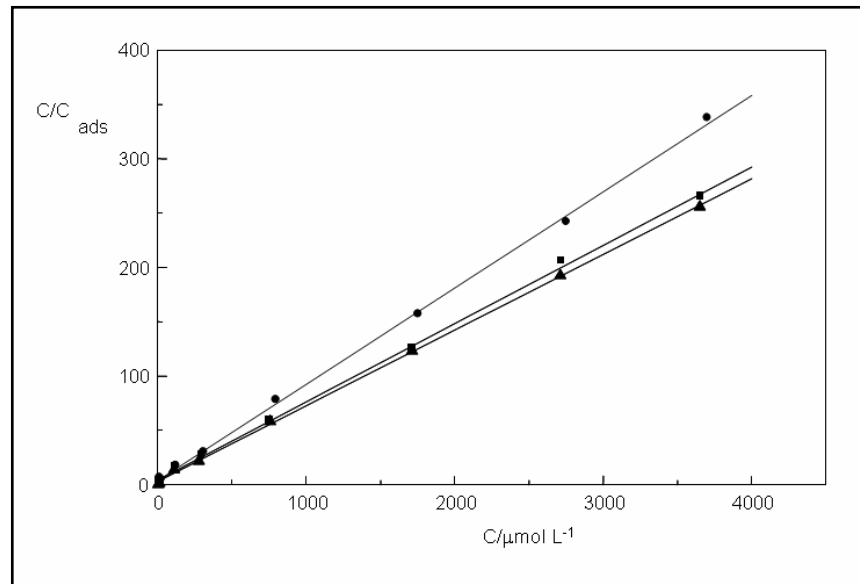Figure 2 shows that the data comply with Eq. (3). The calculated R-values are satisfactory (in all cases R>0.998).

Figure 2. Adsorption of oxovanadium(IV) by hydroxyapatite from aqueous solutions. Plot of the linear equation, Eq. (3). (▲) T = 288 K ; (■) 298 K and (●) 308 K.

This fact together with the structural evidence [22] suggests that the interaction of VO^{2+} with HAP is only restricted to the uptake of VO^{2+} from solution by an adsorption process. In the studied pH range HAP is positively charged and the adsorption of a positive species on it indicates a specific adsorption; thus adsorption occurs by formation of an inner sphere surface complex. Analogous conclusions were put forward by Wehrli et al. [26] for VO^{2+} adsorption onto Al_2O_3. In our case the formation of a surface complex involves the OH group according the equilibrium (1).

Although the Langmuir equation fits the adsorption isotherms measured under all experimental conditions used in this work, the Langmuir model does not describe adequately the adsorption mechanism. Nevertheless, the descriptive capacity and the simplicity of Eq. (1) are appropriate for our purpose.

It can be observed from Table 2 that K decreases when the absolute temperature (T) of the medium increases. This fact indicates that the formation of the surface complex implies a typical exothermic reaction. To obtain the thermodynamic magnitudes (ΔH°_r, standard heat of reaction; ΔS°_r, standard entropy of reaction), which characterize the adsorption process of Eq. (1), the K values were plotted according to the equation of van't Hoff, as shown in Figure 3.

Table 1. Molar concentrations of oxovanadium(IV) related to its adsorption by hydroxyapatite in the interval 288-308 K (pH = 3.5)

C_o $\mu mol\ L^{-1}$	C $\mu mol\ L^{-1}$	C_{ad} $\mu mol\ g^{-1}$	C/C_{ad} $g^{-1}\ L^{-1}$
288K			
60.73	1.39	3.56	0.39
121.46	10.13	6.68	1.51
242.93	110.26	7.96	13.85
485.86	275.86	12.60	21.89
971.73	756.06	12.94	58.43
1943.46	1711.79	13.90	123.15
2944.64	2709.98	14.08	192.47
3886.92	3649.26	14.26	255.90
298K			
60.73	11.73	2.94	3.98
121.46	21.13	6.02	3.51
242.93	119.26	7.42	16.07
485.86	299.19	11.20	26.71
971.73	758.39	12.80	59.25
1943.46	1714.79	13.72	124.98
2944.64	2720.75	13.43	202.59
3886.92	3656.62	13.80	264.97
308K			
60.73	17.06	2.62	6.51
121.46	26.29	5.71	4.60
242.93	124.60	7.10	17.59
485.86	312.36	10.41	30.00
971.73	800.56	10.27	77.95
1943.46	1756.79	11.20	156.85
2944.64	2754.64	11.40	241.63
3886.92	3703.92	10.98	337.33

C_o = initial molar concentration of oxovanadium (IV); C = molar concentration of oxovanadium (IV) in the equilibrium; C_{ad} = moles adsorbed per gram of adsorbent.

Table 2. Adsorption of oxovanadium(IV) by hydroxyapatite: Value of the constants that characterize the adsorption isotherm, Eq. (3).

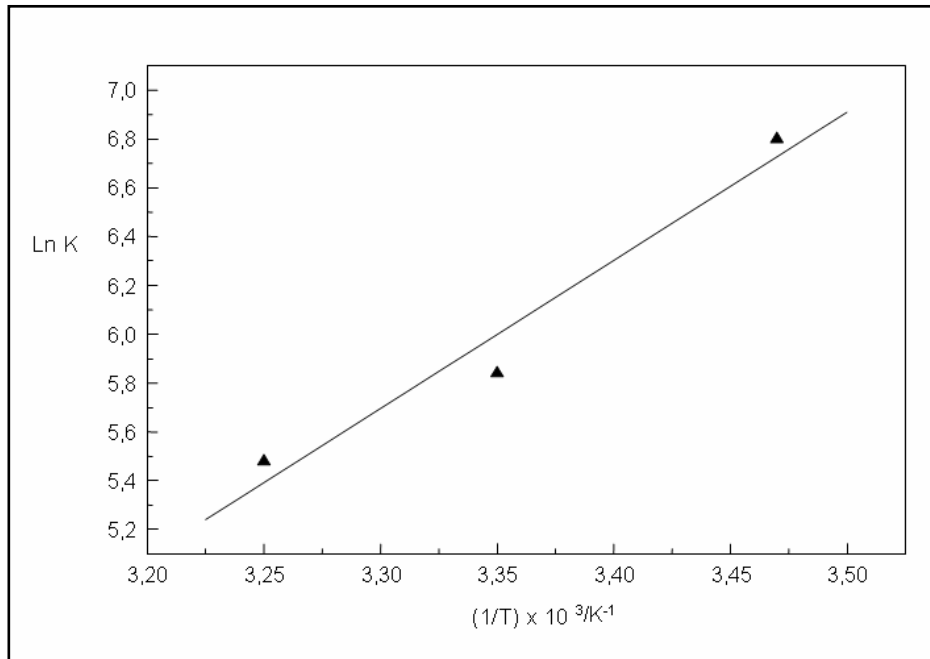| Temperature (K)	L ($\mu mol\ g^{-1}$)	K x 10^2 (L μmol^{-1})
288	13.10	9.04
298	13.48	3.45
308	11.20	2.40

Figure 3. Determination of the standard heat and standard entropy for the adsorption reaction between oxovanadium(IV) and hydroxyapatite by means of the van't Hoff equation.

The following thermodynamic parameters were calculated:

$$\Delta H^\circ_r = -11.8 \text{ kcal mol}^{-1} \quad \text{and} \quad \Delta S^\circ_r = -45.05 \text{ cal mol}^{-1} \text{ K}^{-1}$$

It can be clearly observed that an increase of T values in the reacting medium tends to avoid the occurrence of the adsorption studied reaction.

Kinetics of the adsorption

According equilibrium represented by Eq. (1), it can be proposed the following rate equation:

$$-\frac{d[VO^{2+}]}{dt} = k_1 [VO^{2+}] [\equiv OH] - k_2 [\text{—}OVO^+] [H^+]^n \qquad (4)$$

where k_1 and k_2 are the rate constants of second order (L mol^{-1} h^{-1}) for the forward and reverse reaction, respectively. Several calculations were performed until we found that the proposed adsorption reaction fit to:

$$-\frac{d[VO^{2+}]}{dt} = k_1^* [VO^{2+}] - k_2^* [\text{—}OVO^+] \qquad (5)$$

which can be re-written as:

$$-\frac{d[VO^{2+}]}{dt} = k_1^* C - k_2^* C_{ad} \qquad (6)$$

where k_1^* and k_2^* stand for the rate constants for the pseudo first order reaction (h^{-1}), C is the equilibrium VO^{2+} concentration and C_{ad} is the adsorbed VO^{2+} concentration.

Integration of Eq. (6), taking into account that $C_{ad} = (C_o - C)$ and $k_2^* = k_1^* \dfrac{C}{C_{ad}}$, yields the following linear equation:

$$\ln (C - C_t) = \ln C - \frac{k_1^* C_o}{C} t \qquad (7)$$

where t is the time; C_o is the concentration of VO^{2+} when t=0; and C_t is the VO^{2+} concentration when t=t.

Equation 7 can be re-written as:

$$\ln (C - C_t) = \ln C - k_1^\# t \qquad (8)$$

where $k_1^\#$ is the specific constant rate, which can be obtained by plotting the logarithm of the difference of concentrations, $\ln (C - C_t)$, against the time (t) as shown in Figure 4.

Table 3 summarizes the values of $k_1^\#$ for the three temperatures of work.

Table 3. Values of $k_1^\#$ at the different temperatures.

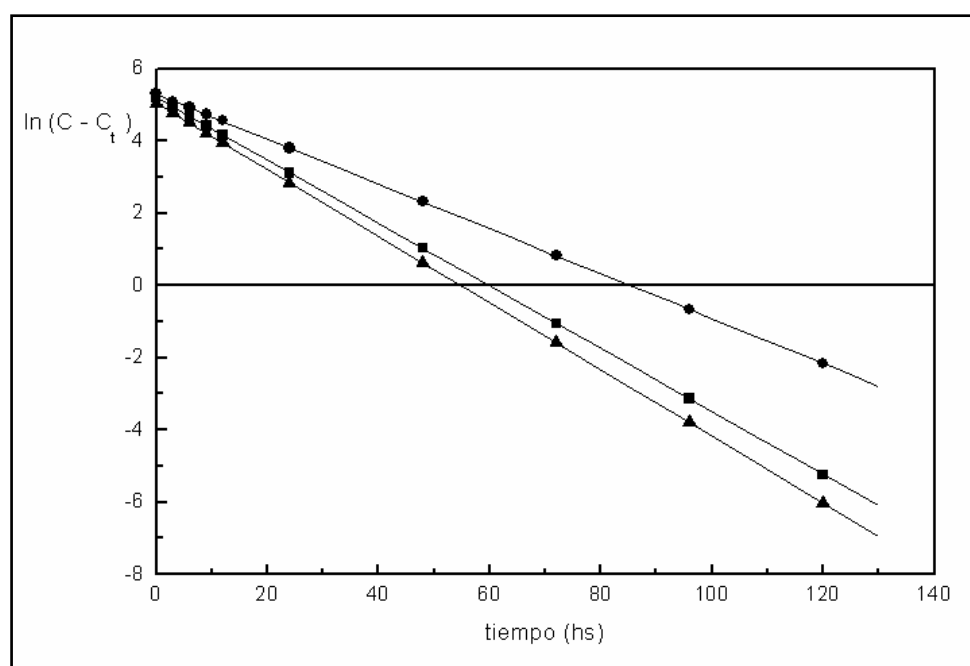| T (K)	288	298	308
$K_1^\# \times 10^2$	6.21	8.68	9.23
Correlation Coefficient (R)	0.9999	0.9998	0.9999

Figure 4.: Variations of the molar oxovanadium(IV) concentration with time according to Eq. (8), at (▲) T = 288 K ; (■) 298 K and (●) 308 K.

The excellent correlation coefficients show that the adsorption reaction follows a kinetic law of order one with respect to oxovanadium(IV) ions.

After the well known Arrhenius empirical relation:

$$\ln k_1^{\#} = -\frac{Ea}{R}\frac{1}{T} + \ln A \tag{9}$$

The obtained values for A (pre-exponential factor, h^{-1}) and E_a (activation energy, kcal mol^{-1}) were:

A = 1114 h^{-1}

Ea = 5,6 kcal mol^{-1}

The high value of the activation energy explains the low rate of adsorption of oxovanadium (IV) on HAP.

Microstructure and EDS analysis

SEM micrographs showing the microstructure of HAP and VO^{2+}- HAP can be seen in Figures 5 (a) and (b). Grain boundaries are visible in both structures at a very high magnification. It is clear that grain size is in the nano range (120-180 nm). EDS analysis clearly shows the presence of V in the adsorbed HAP. The selected sample was obtained from the adsorption experiment at 288 K and pH 3.5.
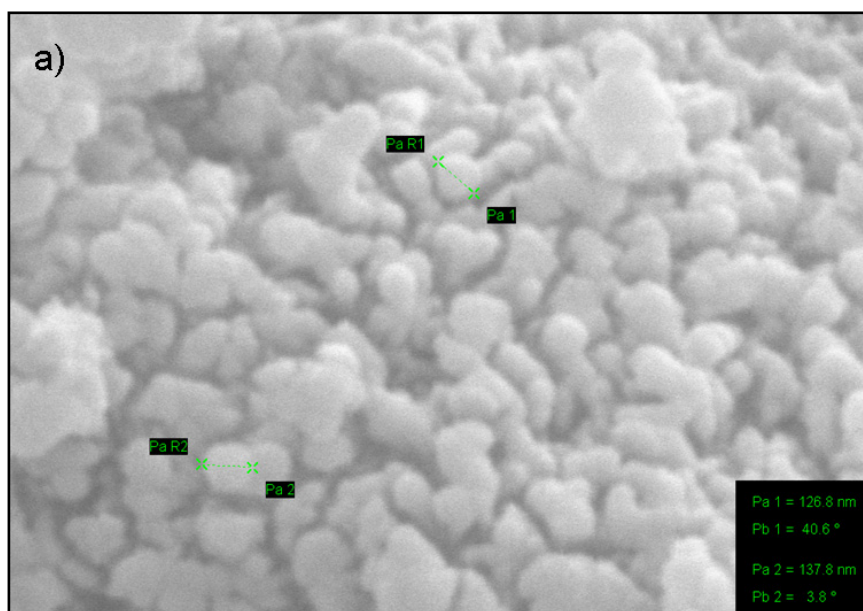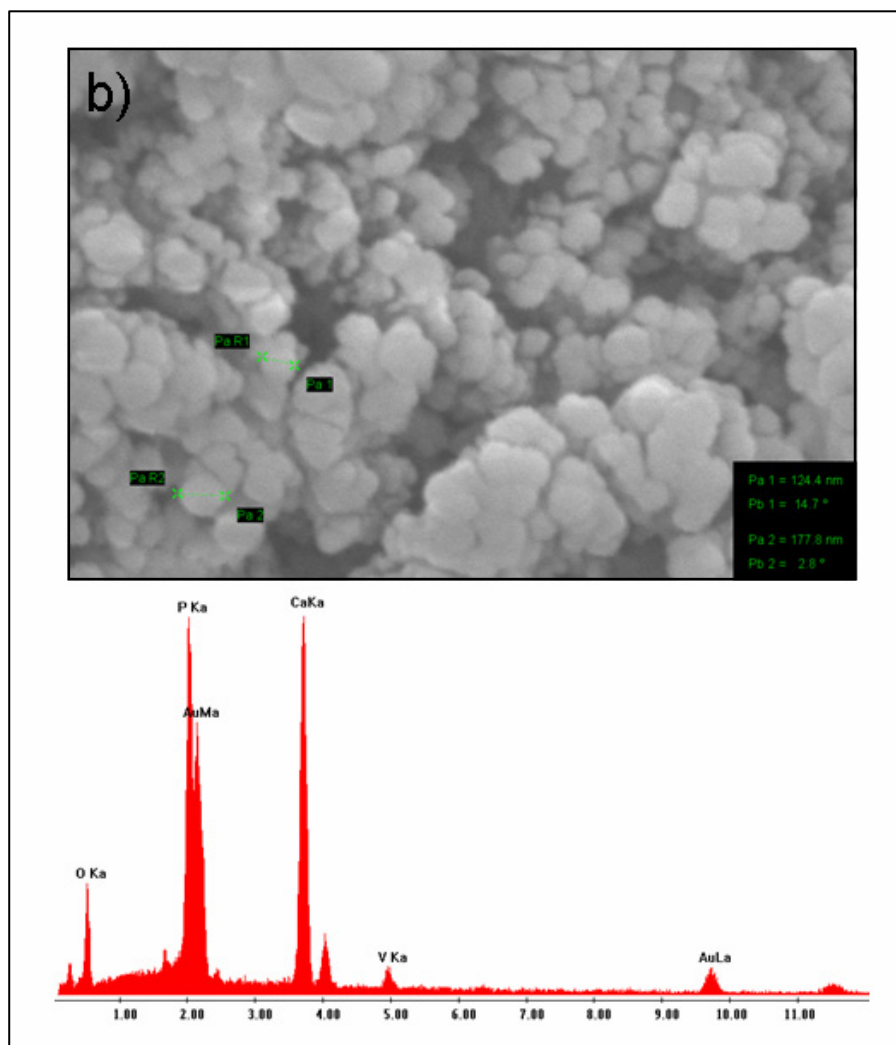
Figure 5. a) Scanning electron micrograph of pure HAP. b) Scanning electron micrograph and EDS plots of HAP after adsorption of VO^{2+}.

Conclusions

We have studied the adsorption process of oxovanadium (IV) ions on synthetic nanoparticulated calcium hydroxyapatite.

The adsorption mechanism can be explained in terms of an association complex that includes the adsorbate and the OH groups belonging to the adsorbent surface.

The Langmuir isotherm fits the experimental adsorption data. The adsorption capacity increases when the temperature decreases showing an exothermic process.

The thermodynamic magnitudes associated with the adsorption process, ΔH^{o}_{r} and ΔS^{o}_{r}, reported here, allowed us to conclude that the proposed model is adequate to describe the VO^{2+}-HAP interaction.

The kinetic experiments carried out at different temperatures indicate that the adsorption reaction follows a kinetic law of order one with respect to oxovanadium(IV) ions. The mechanism

of the global reaction should include a step that involves a reaction between two species of the same charge. The calculated activation energy supports the low rate for the adsorption process.

The experimental data presented in this work contribute to the elucidation of an adsorption mechanism for the studied system and to the better knowledge of the sorptive properties of HAP.

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